

BISMALEIMIDES AND RELATED MALEIMIDO POLYMERS AS MATRIX RESINS
FOR HIGH TEMPERATURE ENVIRONMENTS

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Bismaleimides are being increasingly used as matrix resins for graphite-reinforced composites. The monomers are cured by a thermally-induced addition reaction to give highly cross-linked, void-free network polymers having good physical properties with higher thermal stability, higher char yield, better fire resistance, and lower water absorption than currently used epoxy systems.

There are problems with maleimides, however, such as solvent retention in the prepregs, high temperature often needed for curing, and the brittleness of the polymers due to the high cross-link density obtained in network polymers.

The monomeric bismaleimides are relatively easy to make with a wide variety of structural variation available for property modification. The structural modifications to be described will include a variety of aromatic diamines. Phosphorous-containing aromatic di- and triamines have been made into bis- and trismaleimides to give polymers that will not burn, even in pure oxygen. Some maleimides based on the cyclotriphosphazene nucleus give good polymers having excellent thermo-oxidative stability as measured by high char yields in air at 700 °C.

Other modifications that will be described are those that are designed to improve the fracture toughness. The diamines, for instance, can be extended by reactive dianhydrides to give lengthened bismaleimides. By decreasing the cross-link density, the brittleness is expected to be reduced. Some of the systems described have also been modified by reactive elastomers to impart toughening.

Coreaction of bismaleimides with other thermostable reactive monomers such as vinylstyrylpyridines or stilbazole combine the good properties of both types of resins with a lowering of the curing temperature required. Among some of the maleimide resins it is possible to find systems that will be useful for continuous service at 300 °C (570 °F).

INTRODUCTION

This paper reviews some of the important structure-property relationships that exist for bismaleimides and related polymers as they influence the potential application of this class of polymers when used as matrix resins for fibrous composites in high-temperature environments. Of special interest is the use of these polymers as binders for fire-resistant secondary lightweight composites for aerospace application. Some consideration is given to the potential application of this class of resins for long-time use as secondary structures and as elastomeric-toughened primary structures at temperatures in excess of 300 °C. The advantages and limitations of state-of-the-art bisimides with respect to high-temperature use, fireworthiness, processability, and environmental stability are described.

Polymers have been prepared by modification of the basic maleimido structures and by polymerization mechanisms which eliminate thermally-weak bonding units. Easily thermally degraded aliphatic linkages (also contributing to brittleness) and pivotal groups such as methylene and isopropylidene have been replaced with phosphonates and cyclotriphosphazenes. Virtually completely fire-resistant polymers with limiting oxygen indices of 100 have been obtained. The effect of microstructural changes on the pyrolysis mechanisms in both inert and air environments has been demonstrated. Polymers have been found with residue weights in excess of 80 percent in air at 700 °C. Substantial retention of mechanical properties suggests a new upper limit for polymer application. The role of residual solvent on high-temperature properties of bismaleimides has been found to be extremely deleterious. Hot-melt systems have been devised by chain extension and copolymerization with reactive oligomers to eliminate the use of solvent and to reduce the cure temperature and internal strains.

A key objective of this paper is to introduce a new class of bisimide copolymers derived from the polymerization of vinyl stilbazole oligomers which can be processed without solvent, cured under somewhat lower temperature conditions than standard epoxides (165 °C), and gives a resulting matrix resin with a glass-transition temperature and polymer decomposition temperature in excess of 400 °C. It appears that the stilbazole chain unit provides a thermally-stabilizing effect on the aliphatic linkage resulting from the vinyl addition polymerization as well as a "buried" or thermally-reactive functionality to cross-link the polymer at temperatures in excess of 500 °C. This results in the high char yield (50 percent or greater) needed for fire resistance but allows for greater chain flexibility at use temperatures. This unique combination of bismaleimide and vinyl stilbazole as addition copolymers provides a wide range of formulation possibilities to tailor the matrix resin to a variety of high-temperature and fire-resistant applications.

Bismaleimides

Generically, these polymers refer to those matrix resins for application in fibrous composites which contain at least two maleimido groups prepared through the reaction of maleic anhydride. Generally this is a two-step reaction involving the formation of an amide acid intermediate followed by ring closure to give maleimido end groups. Primary aromatic diamines are shown in figure 1. The resulting oligomers are soluble in acetone, tetrahydrofuran, and N-methylpyrrolidone. As simple bisimide derivatives of aromatic diamines they are generally high-melting solids of low viscosity which polymerize rapidly at temperatures slightly above their melting point. When fully cured these simple bisimides exhibit high glass temperatures in excess of 350 °C, and anaerobic char yields greater than 60 percent, but are extremely brittle due to their high cross-link density.

These polymers made a brief appearance in the late sixties for applications requiring somewhat higher-temperature resins than conventional epoxides for glass-fiber reinforced composites. There is a very limited need for matrix resins, with modest improvements in thermal stability when compared with epoxy resins. Simple bisimides, such as those derived from methylenedianiline with a melting point of 202 °C, are soluble in polar solvents and are extremely difficult to process as mentioned above. For these reasons they found no significant application. However, these simple bisimides exhibit high char yields of 60 to 70 percent as measured anaerobically at 600 °C with very little thermoplasticity in the fire environment. It has been a major objective of current research to overcome the limitations of processing and brittleness of bisimides and at the same time retain the excellent fireworthiness and high-temperature stability of the basic bisimide system.

Several modifications of bisimide structure have appeared commercially. The Keramide resin systems presumably take advantage of the opportunity of adding an aromatic amine across the maleimido double bond to introduce an aliphatic secondary amine bridge, as shown in figure 2. This reaction increases the molecular weight of the bisimide precursor and introduces a point of chain flexibility. One observes easier processability, lower melting point, better solubility, more controlled viscosity, and reduced cure rate (better reaction control). The chain extension also reduces the glass temperature and inherent brittleness to some degree. Keramide 601, which is typical of this class of bisimide modification in fiber-glass composites, is probably good for continuous application at 150 °C for 50 000 hr with good electrical properties. It has found wide use in circuit board applications and in some cases may be preferred over epoxy resins. The presence of the Michael addition product introduces a point of thermal instability in the imide chain which suppresses the char yield and thermal stability, thus impairing the use of this class of resins in high-temperature and fire-resistance applications.

A second modification of the microstructure of bisimide matrix resins is found in M-751, as shown in figure 3. There the bisimide prepolymer has been chain extended by increasing the chain length of the diamine by the reaction of p-phenylene diamine with m-aminobenzoid acid, giving the bisimide shown as B. In addition, the prepolymer is further chain extended by including an equal molar amount of an amine-terminated maleimide which also reacts in situ by Michael addition. This so called "eutectic" mixture increases molecular weight, reduces the melting point, increases viscosity, and moderates the reactivity of the maleimido double bond during processing. As will be seen, this molecule still has several points of thermal instability; the Michael product and the phenylene-methylene bridge. Although the aromatic amide reacts at high temperature to eliminate water and hydrogen, it appears that the carbon-nitrogen bond is retained. As a consequence, M-751 is characterized by a high anaerobic char yield of greater than 60 percent.

This class of polymers has two specific limitations for use as easily processable high temperature resins. In figure 4, the results of the differential scanning calorimeter, DSC, are shown. An endotherm at 125 °C characterizes the melting point and an exotherm at 275 °C displays the DSC curing temperature. The melting point and viscosity of the melt taken together do not permit hot-melt processing as solvent is required. The high temperature needed to fully cure M-751 (275 °C) limits its use in conventional composite processing where cures at 160 °C are more appropriate.

In 1976 Kourtides et al. (ref. 1) demonstrated the unusual fire resistance of M-751 in secondary composite structures intended for application as interior panels for mass transportation. Parker (ref. 2) showed that the anaerobic char yield in the range of 45 to 65 percent accounted for a unique and optimized combination of flammability and ablation properties. This optimized combination of properties in secondary structures such as interior panels gave rise to a maximum time to flash-over and minimum smoke and toxic gas emissions, as well as good fire-retardant properties.

Table 1 compares the relative ranking of the flammability characteristics, the limited oxygen index, and the percent optical transmission with the measured anaerobic char yields of M-751, H-795, and other matrix resin polymers. It can be seen that the improvement of bismaleimides is some two to three times better than the epoxide-based composite system. The same relative ranking of flammability is seen in both glass and graphite compositions.

The high-temperature pyrolysis reactions occurring in one flaming combustion mode have been found to correlate rather well with the anaerobic char yield at 600 to 800 °C. As will be seen, there are parallel correlations with polymer decomposition temperatures and glass temperatures of some systems. Anaerobic char yield alone should not be used as a criterion for high temperature thermo-oxidative stability. The general quantitative pyrolysis reactions of simple bisimides can be simply accounted for by ring coalescence of the aromatic and bisimide rings with the elimination of water and hydrogen. The resulting carbon-nitrogen ring system is usually stable in air up to 400 °C and is rapidly oxidized to zero char yield at temperatures greater than 500 °C. Fortunately, in the fire case the rate controlling pyrolysis reactions take place in an essentially anaerobic environment where the effect of thermo-oxidative stability is minimal.

As will be seen, phosphorous modification of the maleimido matrix resins provides both thermal and thermo-oxidative stabilities. The only factor which limits the general acceptance of M-751 and H-795 bismaleimides for superior fireworthy composite structures is the high temperature required for curing compared with standard epoxy systems.

Structural Composites from Maleimido Matrix Resins

Bismaleimides cure without the evolution of small volatile molecules by the thermal polymerization of the maleimide double bond. This feature of these molecules is a significant advantage in obtaining void-free composites. Thermal degradation induced by "backbiting" reactions of unreacted amino and carboxylic acid groups is virtually eliminated.

Unfortunately, as pointed out above, the poly-addition reaction exhibits a DSC curing reaction at 275 °C. In curing 9-ply satin-weave graphite composites, this reaction temperature extrapolates to temperatures of 220 to 240 °C for 2 to 3 hr and still may require further postcure to realize the potential mechanical properties.

In addition to causing higher processing costs than standard graphite epoxides, these higher cure temperatures can produce large internal strains in standard bisimide composites. It has been observed that these high internal strains encountered in large graphite composites can induce the formation of intolerable concentrations of microcracks with catastrophic loss of impact properties uncharacteristic of small laboratory samples. It has been found that addition of small amounts of liquid elastomer of the order of 2 to 3 percent (not conventional rubber toughening) gives acceptable composites free of microcracks, resulting in nominal impact resistance.

What is needed is an alternative curing mechanism for bisimide structures which will permit lower-temperature processing and still not interfere with the inherent thermal stability of the aromatic bisimide ring system. This question will be taken up in detail in the next section.

Processing Conventional Bisimides

Up to this point, bismaleimides made processable by chain extension through thermally-weak links and requiring solvent-based varnishes to prepare prepregs have been considered for fire resistant secondary structures used under ambient conditions. It has been found that under normal processing conditions it is virtually impossible to remove the last traces of solvent (between 1 to 3 percent) from the

cured graphite composite, as shown in figure 5. Here it can be seen that the steady-state concentration of solvent, in this case NMP, decreases with increasing temperature but is never completely eliminated (ref. 3).

The effect of this residue of solvent, which appears to plasticize the M-751 (shown as bismaleimide A in figure 6), is catastrophic. Here the loss in modulus is plotted as a function of test temperature. It can be seen that the compressive modulus (also true of ultimate strength) decreases very rapidly with temperatures from room temperature to 300 °C. Here the bisimide A composite has lost better than 60 percent of its initial properties.

Initially the graphite composite is equivalent to the epoxy resin. At elevated temperatures, however, it is no better than the epoxide. This result is compared with the phenolic resin which shows no loss in properties over the entire temperature range. In fact, the phenolic resin shows an upward turn in the compressive modulus due to further curing above 250 °C.

It can be concluded from these results that although the bisimide A is thermally and oxidatively stable to 250 to 300 °C (unlike the epoxide which is thermally degrading in this temperature range), bisimide A has no better performance than the epoxide due to adventitious solvent. It is clear from the foregoing result that primary structural composites for use at temperatures around 300 °C cannot easily be formulated from useful solvent systems.

What is needed is a processable bismaleimide in the form of a hot-melt system to eliminate both the need for solvent application and chain extension by a more thermally-stable chain extension mechanism than the Michael addition product. Bisimide H-795 fulfills these requirements. The general structure for this hot-melt bisimide is shown in figure 7. Here the simple aromatic bisimide has been chain extended to double the molecular weight by eliminating the thermally-weak chain links present in M-751, thus reducing the comparable melt viscosity and providing an easily processable melt at 120 °C.

The compressive moduli for comparable structural graphite composites are plotted as a function of temperature in figure 8. Here it can be seen that the hot-melt bisimide H-795 (bisimide B composite) retains its mechanical properties without change to 300 °C at which point both epoxy and bisimide A have completely degraded.

From these data alone it is not possible to distinguish between solvent effects and chain degradation. Both degradation processes and plasticization are involved in the failure of bisimide A to perform at high temperatures. It is clear from the foregoing that high-temperature structural composites from bisimide systems will probably evolve from hot-melt systems containing no common aliphatic bridging units.

Recently it has been observed that bismaleimides in general have been found to exhibit significantly better hot-wet strength than comparable graphite epoxy systems. The effect of bisimide structure on moisture absorption was examined by simple immersion tests of both neat resins and graphite composites formulated from the neat resins. The room temperature water absorption data is plotted in figure 9. Here it can be seen that the water absorption for bisimides is much slower initially than that of standard epoxides, but eventually they attain values quite comparable to the epoxy resin. This is not true for the formulated composite. The rate of water absorption for bisimide B, the more polar hot-melt

bisimide, is comparable to the rate of absorption of the epoxide. The more aliphatic bisimide has a very low water absorption and equilibrium value. It is conjectured that the reported excellent hot-wet strength for current bisimides is determined in large measure by the polarity of the bisimide molecular unit, low initial rate of water absorption, and the fact that water may be less effective as a plasticizer for bisimide structures.

Even with the advantages of the hot-melt bisimide B (H-795), it still exhibits a DSC cure temperature of 275 °C and all the limitations these cure conditions impose. Matrix resins are desirable as alternatives to epoxide polymers for advanced aerospace composite structures. These are known by NASA as the second generation matrix resins. With the limitations previously outlined, it is clear that contemporary bisimides do not meet these needs.

It is well known that vinyl monomers such as styrene and divinylbenzene readily copolymerize with maleic and fumaric acid derivatives at low temperatures from 120 to 150 °C. Peroxide catalysis of this reaction forms the basis for polyester laminate technology. It has also been found that styrene, for example, readily polymerizes with phenylmaleimide to give high molecular weight linear polymers which are initiated thermally or with peroxides. It is reasonable to expect that vinyl monomers and a wide variety of vinyl-terminated oligomers would be expected to act as reactive diluents or comonomers for maleimido oligomers.

The objectives for an optimum liquid oligomer and bismaleimide copolymer are outlined in table 2. Processing as a hot melt and curability with a vinyl oligomer theoretically should present no particular difficulty. However, simple vinyl monomers should be expected to give difficulties as a result of volatility; that is, microvoid formation and volatile losses. The simple aliphatic vinyl linkage should be expected to degrade the high-temperature performance by depolymerization and scission, thus limiting high-temperature stability and substantially reducing the anaerobic char yield, which reduces flammability. It is extremely unlikely that any simple vinyl-hydrocarbon monomer can be found as a copolymer reactant which can meet the objective criteria set forth in table 2.

Earlier (ref. 3) it was shown that graphite composites formulated from polystyrylpyridine matrix resins, obtained from the condensation reaction of collidine and aromatic dialdehydes, give the best fire endurance and high-temperature stability of any matrix resin yet evaluated. Unfortunately, because of the elimination of water in condensation curing reactions, void-free composites are difficult to obtain. Also, extremely vigorous curing temperatures above 250 °C are required. Short-term high-temperature stability at temperatures in excess of 400 °C have been observed. It is believed that the matrix resin is stabilized by the presence and persistence of the double bond of the conjugated stilbazole group at temperatures up to 400 °C. From model compound studies (ref. 4), it appears that the stilbazole group reacts in situ to give a highly cross-linked ring system, characterized by char yields of 70 to 80 percent at 600 to 800 °C in nitrogen.

The special thermal properties of the stilbazole double bond have been taken advantage of in the design and synthesis of the two types of liquid oligomers shown in figure 10. Earlier attempts (ref. 5) to synthesize vinyl-terminated linear stilbazoles from dimethylpyridines such as lutadine did not meet the criteria for epoxide resin replacement.

The two types of oligomers shown in figure 10, however, seem to meet these needs. 5-vinyl-2-methylpyridine gives a low melting (40 °C) oligomer, suitable for copolymerization with a wide variety of maleimido prepolymers. A chain-extended

version obtained with collidine is also shown in figure 10. Vinylstyrylpyridine, VPSP, has been prepared from collidine, terphthaldehyde, and 5-vinyl-2-methylpyridine. Both comonomers have been easily thermally polymerized with the hot-melt bisimide, H-795, over a wide range of comonomer ratios.

Typical thermal processes occurring during these copolymerizations are shown for the case of VST and H-795 in the differential scanning calorimeter traces in figure 11. Here the heat flow is plotted as a function of temperature. It can be seen that the VST oligomer exhibits a DSC melting temperature of 50 to 60 °C with a slow and weak exothermic curing reaction occurring over a temperature range from 160 to 240 °C, due to the thermal polymerization of the vinyl double bond. In separate thin-film IR studies it has been shown that the stilbazole double bond does not participate in this reaction. Another mild exotherm becomes apparent above 322 °C, probably associated with limited polymerization of the stilbazole double bond.

A similar thermal history is shown in figure 11 for the bismaleimide hot melt, H-795. The DSC shows an endothermic melting point around 118 °C and a DSC cure temperature of 282.4 °C, typical of aromatic bismaleimides. It can be seen that the copolymer formulated from a mole ratio of 3:7 of VST to H-795 begins to melt around 50 °C and then polymerizes rapidly at 164 °C, a cure temperature some 120 °C less than pure bismaleimide. Similar reductions in melting points and cure temperatures are seen with VPSP/H-795 copolymers.

The results obtained from the thermochemical-physical characterization of this new family of copolymers are compared in table 3. It can be seen that in all of the copolymer ratios investigated, the cure temperatures are significantly reduced below those required for the bisimides and in most cases less than those required for aerospace-grade epoxides (MY-720-DDS). As might have been anticipated, the degree of cure temperature reduction changes monotonically with the concentration of vinyl double bonds contributed by the VSP or VPSP in the bismaleimide copolymer. It is interesting to note that the glass temperatures of these copolymers, as measured by dynamic mechanical analysis, is 380 °C or higher in all cases; that is, several hundred degrees higher than the cure temperature of 160 to 200 °C. The anaerobic and high temperature stability in all cases is at least equivalent or better than the bisimide alone, as indicated with polymer decomposition temperatures in excess of 400 °C. As predicted from studies on other stilbazole polymers, the anaerobic char yields are significantly higher than those possible from aerospace-grade epoxides.

With the exception of the high VST ratio of 3:7, all the measured char yields of these copolymers are substantially higher than the H-795 bismaleimide alone. It is probable that the 3:7 copolymer has too low a cross-link density to effect optimum char yield.

As mentioned previously, the parallelism that exists among char yield, glass temperature, and thermoplasticity at 300 °C is clearly apparent in the results shown in table 3. It can be seen that the dynamic modulus from DMA measurements of the low-temperature cured copolymers in typical graphite-composite formulations remains unchanged from room temperature to 300 °C. The long-term thermo-oxidative stability of these new graphite composites remains to be examined.

A preliminary evaluation of the mechanical properties of these new copolymers as matrix resins for graphite composites was performed on simple 8-ply satin-weave graphite fabrics with resin contents from 26 to 32 percent. The results are shown

in table 4, compared with an H-795 control. It can be seen that the flammability of the composites based on the copolymers is better than the bisimide alone. It is also obvious that the copolymers give both short-beam shear and strength values two to three times greater than the bisimide alone. No attention has been given to optimizing the fiber sizing or polyphase matrix toughening to improve damage tolerance or impact strength.

It should also be noted that the use of vinyl-terminated stilbazole oligomers may be applied generally to a variety of heretofore difficult bisimides. The values for water absorption after 2 hr in boiling water are also given in table 4. The absorption amounts to 1 percent or less. It has been found that comparable epoxy-graphite composites usually absorb 2 to 3 percent under similar conditions. One may expect substantial improvement in the hot-wet strength of these composites.

Here, then, is a nonpolar (no oxygen), low-temperature curing oligomer which reduces water absorption, gives a threefold improvement in mechanical properties, requires no solvent, gives char yield consistent with optimum fire resistance, and has service temperatures of 300 °C or better. It is believed that the vinyl stilbazole copolymers described in this paper represent a significant advance in matrix resins for graphite secondary structures, where ease of processing, fireworthiness, and high-temperature stability are product requirements. Further research is necessary to evaluate the toughness and impact resistance of these copolymers as matrix resins for primary structure.

In the case of high-temperature, speciality graphite-composite structures, where economic considerations of materials and processing can be relaxed for performance, maleimido matrix resins can be modified to give very thermally-stable polymers. These polymers are good for continuous service at 300 °C or better and have complete fire resistance, limiting oxygen index of 100, and mechanical properties superior to the best graphite-epoxy composites.

Two structural changes in state-of-the-art bisimides must be met. First, the bond strength of the pivotal aliphatic carbon bridge must be replaced with a more thermal-oxidative resistant group than an aliphatic carbon. Secondly, the cross-link density must be reduced by chain extension to overcome the brittleness of the matrix resin.

As shown in figure 12, two bismaleimide matrix resins have been prepared by replacing the usual methylene bridge with phosphonate linkages (ref. 6). In resin 1 the methylene bridge has been replaced by an aminophenylphosphonate and in resin 2 it has been replaced with methylphosphonate. These two polymers were rubber modified with ATBN and the perfluoroalkylene diamine shown in figure 12. Resin 1 was formulated with ATBN between 3.9 and 18 percent. Even small additions of ATBN degrade the fire resistance and high-temperature stability of the neat resin. Thermogravimetric analysis of all of these modifications gave polymer decomposition temperatures above 350 °C and anaerobic char yields between 47 and 71 percent. Addition of 6.4 percent of the perfluoroalkylene diamine (3F), shown as g in table 6, had little or no effect on the neat resin char yield and still resulted in polymers with an LOI of 100.

The effect of the perfluoroalkylene ether modification on the mechanical properties of bisimide II are shown in table 7. It can be seen that with exception of the LOI and flexural modulus, this chain extension reaction gave a substantial improvement in all the mechanical properties as compared with the control, and substantially better properties than the composite derived from MY-720 cured with DDS.

An alternative scheme for enhancing the stability of maleimido matrix resins involves replacing the connecting atoms with a thermally stable moiety, in this case the tricyclophosphazene shown in figure 13. Here the resulting hexamine is capped with three maleimido groups leaving three amino groups for chain extension. Other variations of this modification are shown in figure 14 (ref. 7).

As shown in figure 15, all of the maleimido tricyclophosphazenes show polymer decomposition temperatures well over 350 °C in air. High char yields (greater than 80 percent) are again observed with these phosphorous comodified polymers. Both resins I and II gave residue polymer weights between 40 and 70 percent in air up to 800 °C. All organic matrix resin systems examined to this point gave essentially zero char yields in air at temperatures between 500 to 600 °C. These results suggest unexpected thermo-oxidative stabilization of the bisimide system by these phosphazene modifications and may provide a matrix resin for short-term use under rather severe thermo-oxidative conditions. The details of these thermo-chemical reactions of phosphate bisimides remain to be resolved.

What is again remarkable, as in the case of polymer VI which is readily soluble in methylethylketone and gives tough polymer films when polymerized at 250 °C, is the fact that the polymer shows a char yield of 80 percent; a new pyropolymer relatively stable in air at 800 °C is formed. This film, although somewhat brittle, exhibits good semiconducting properties with resistivities in the range of 10 ohm-cm.

The char yields of these tricyclophosphazenes in nitrogen at 800 °C and in air at 700 °C illustrate the unusual thermo-oxidative stability of this new class of maleimide resins. Figure 16 compares these resins with various state-of-the-art bisimides and other aromatic matrix resin polymers with anaerobic char yields in excess of 40 percent. Only the phosphorous-modified polymers give substantial pyrolysis residue weights in air at 700 °C. One may speculate at this point that it may be practical for some purposes to postcure composites derived from silicon carbide fibers at temperatures between 600 and 700 °C to obtain composites suitable for continuous service in air at temperatures above 500 °C.

Finally, figure 17 shows the results obtained by isothermally aging thin films of resin VI in air and nitrogen. These films were cast from MEK and cured at 220 °C. Even with this limited degree of cure there is no weight loss in N₂ up to 72 hr at 350 °C. These data suggest that this polymer may provide continuous service in air at 300 °C. For compositions which can tolerate up to 10 percent weight loss this temperature might be extended to 350 °C.

Concluding Remarks

It has been shown that significant processing and property improvements can be achieved by copolymerization of state-of-the-art bisimides with various vinyl stilbazole derivatives to give both fire resistance and high-temperature properties from hot-melt compositions. Significant improvement in mechanical properties has been achieved through these modifications which may make these new matrix resins ideal candidates for fireworthy secondary graphite composite structures. Phosphorous modifications of maleimido polymers through phosphonate structure and tricyclophosphazene derivatives have provided families of new matrix resins for short-time applications in severe thermo-oxidative environments. With further research these may provide matrix resins for long-term thermo-oxidative stability of advanced composites at temperatures up to 400 to 500 °C.

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Notice

Reference to a company or product name does not imply approval or recommendation of any of the products stated in this paper by the National Aeronautics and Space Administration to the exclusion of others that may be suitable.

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TABLE 1. - RELATIVE RANKING OF GRAPHITE FABRIC
(W-133) COMPOSITES BASED ON
FLAMMABILITY PROPERTIES

Resin	LOI	%T	Resin Y _c 800 C, N ₂	Average, %
Polyphenylsulfone (RADEL 5000)	52	92	47	90.4
Phenolic-Novolak (MXG-6070)	50	92	46	88.7
Benzyl (WRF-1200)	49	81	53	88.1
Polyethersulfone (P-300)	54	74	40	81.4
Bismaleimide B (H795)	56	54	49	80.3
Bismaleimide A (M-751)	47	23	50	64.4
Phenolic-Xylok (Xylok 210)	46	1.5	46	53.5
Epoxy (Control) Fiberite 934	41	1.8	21	36.7

$$\text{AVERAGE \%} = \left(\frac{\text{LOI}}{\text{LOI}_{\text{max}}} \right) 100 + \frac{100}{10 \left(\frac{D_s}{132} \right)} + \frac{Y_c}{Y_{c_{\text{max}}}}$$

%T = % Optical
Transmission

Y_c = % Char Yield

TABLE 2. - OBJECTIVE FOR SECOND GENERATION COMPOSITE-LIQUID
OLIGOMER AND BISMALIMIDE COPOLYMERS

Processability	Hot melt (melting point is less than 130°C) Soluble in low boiling solvent Low gel temperature (<120°C) and time (1/2 hr)
Easy to cure	Low cure temperature (350°F) and time (less than 4 hr)
Impact resistance	Less than 10% shear strength loss after impact with 10 in-lb
High temperature stability	Decomposition temperature is higher than 300°C
Fire resistance	LOI is greater than 40

TABLE 3. - COMPARISON STATE OF THE ART MATRIX RESINS WITH
VST/BMI AND VPSP/BMI COPOLYMERS

Resin System	Cure temperature (DSC Peak), °C	T _g °C	PDT (N ₂) °C	Char yield %	Composite modulus GPa	
					25°C	300°C
Epoxy (MY720)	255	250	300	30	13.5	2
Bismaleimide (H795)	282	>400	400	42	15	14
Copolymers:						
VST:H795 = 1:4	197	380	400	43	13	12
VST:H795 = 3:7	164	----	400	36	----	--
VPSP:H795 = 1:9	245	>400	400	43	17	16
VPSP:H795 = 1:4	230	>400	400	50	15.5	15
VPSP:H795 = 3:7	226	----	400	55	---	--

TABLE 4. - PRELIMINARY MECHANICAL PROPERTIES ASSESSMENT OF VST,VPSP/BMI COPOLYMER COMPARED WITH H 795 IN GRAPHITE FIBER COMPOSITES

Physical and mechanical properties	Resin system with 9ply satin weave graphite fiber				
	H 795	VPSP/H795 1:4	VST/H795 1:4	VST/H795 3:7	VPSP
Resin content %	30.5	26	30	31.5	26
Density, g/cc	1.55	1.43	1.39	1.38	1.44
LOI	52	62	46	-----	57
Water absorption, % 2 hrs boiling water	0.72	1.17	0.99	0.86	1.36
Short beam shear R.T. ksi	1.7	2.95	2.96	2.89	3.15
R.T. flexural: modulus, msi	7.7	7.3	7.3	7.4	7.6
Strength, ksi	24	41	46	41	49
Flexural, 100 °C modulus, msi hot-wet	-----	-----	-----	-----	-----
Strength, ksi hot-wet	-----	-----	-----	-----	-----

TABLE 5. - PROPERTIES OF LIQUID OLIGOMER-BISMALEIMIDE SYSTEMS

Low cure temperature	170 °C
Low gel temperature	110 °C
Low gel time	15 min
Long pot life at room temperature	3 months
High glass transition temperature	>350 °C
High stiffness modulus	>13 GPa at room temperature
High fire resistance	LOI is above 45
Use no solvent (hot melt) or low boiling solvent (THF) for prepreg	-----

TABLE 6. - THERMAL CHARACTERISTICS OF MODIFIED
BISIMIDE RESINS

Sample	Resin and elastomer	Char yield, %* neat resin	LOI, % O ₂ laminate
a	I (control)	61	100
b	II (control)	71	100
c	I + 3.9 % ATBN	58	---
e	I + 18 % ATBN	47	85
f	I + 6.4 % 3F	56.5	100
g	II + 6.4 % 3F	68	100

*In N₂, at 800°C.

TABLE 7. - PROPERTIES OF PHOSPHORYLATED BISIMIDE II MODIFIED WITH
ELASTOMER 3F

Property	Bisimide II		Epoxy*	Percent improvement	
	Control	+6.4% 3F		Over control	Over epoxy
Flexural strength x10 ³ , psi	109.45	138.64	92.26	+26.7	+50.3
Flexural modulus x10 ⁶ , psi	19.4	20.04	7.1	No change	+182
Energy, ft-lb	28.3	41.3	---	+45.9	---
Tensile strength, x10 ³ , psi	59.8	76.9	82.6	+28.6	-6.9
Shear strength x10 ³ , psi	5.38	10.2	7.74	+89.6	+32.5
LOI, % O ₂	100	100	36	No change	+++
Resin content, %	18-20	22.5	25.3	-----	-----
Resin char yield, %	71	68	20	-4.2	-----

*MY 720 cured with DDS

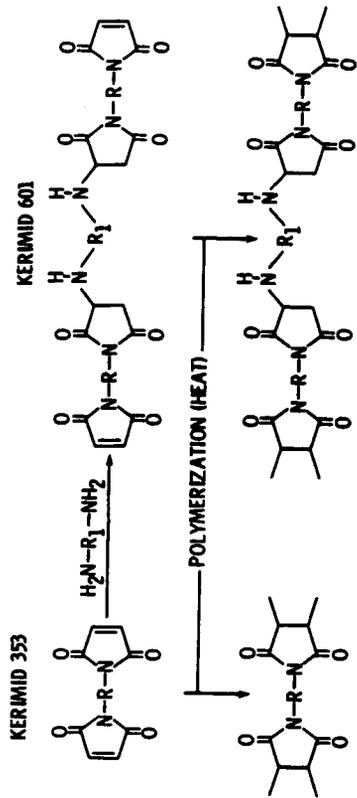
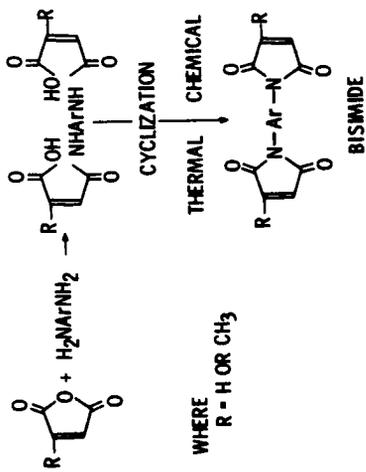


Figure 1. - General synthesis of an aromatic bisimide.

Figure 2. - Chain extension of bisimide by amine addition to double bond (Michael addition).

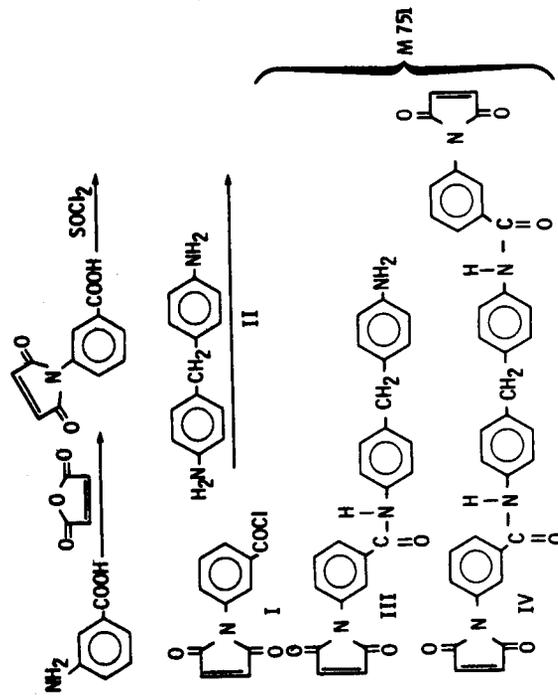


Figure 3. - Chemistry of M 751 resin.

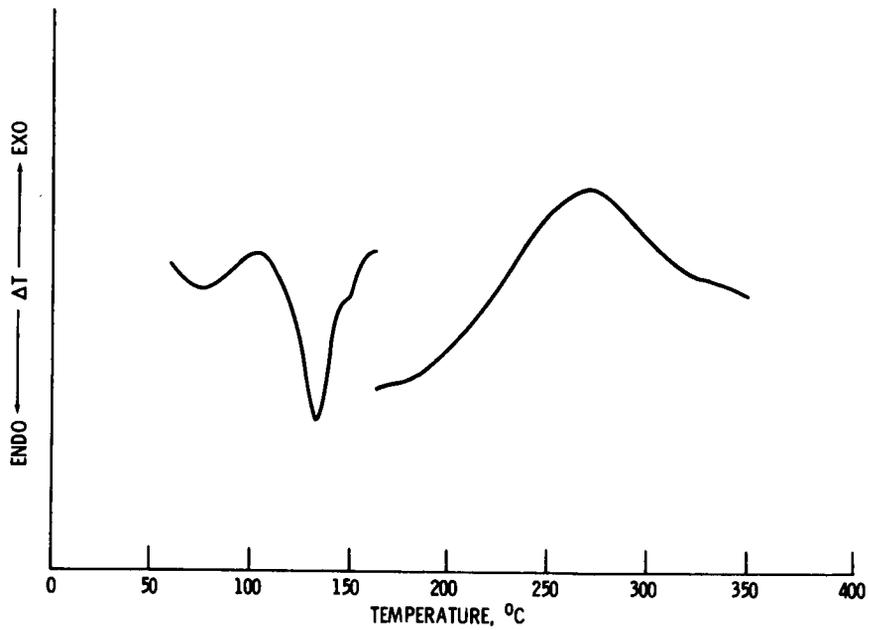


Figure 4. - Melting and polymerization behavior of bismaleimide resin M 751.

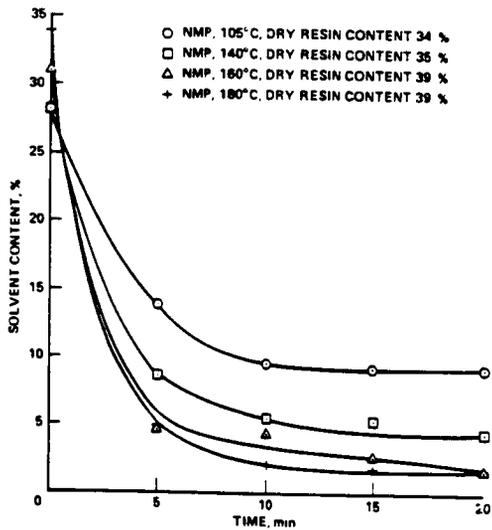


Figure 5. - Plot of solvent content as function of time showing remaining traces of solvent.

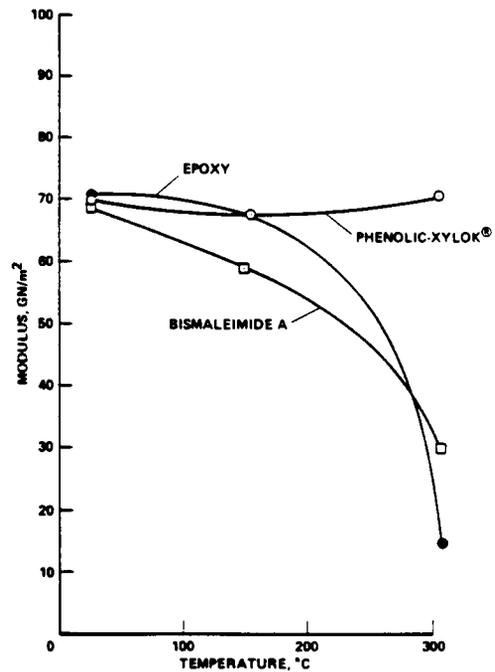


Figure 6. - Plot of modulus as function of temperature showing the decrease in modulus from room temperature to 300 °C.

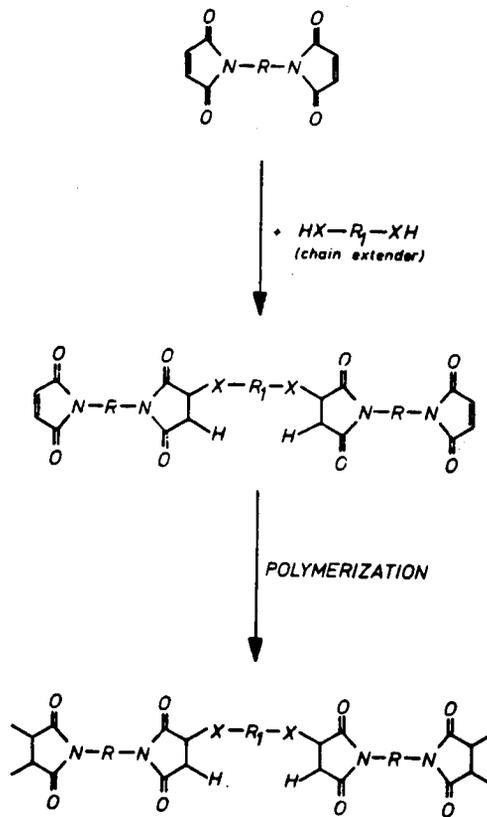


Figure 7. - Chemistry of H 795 resin.

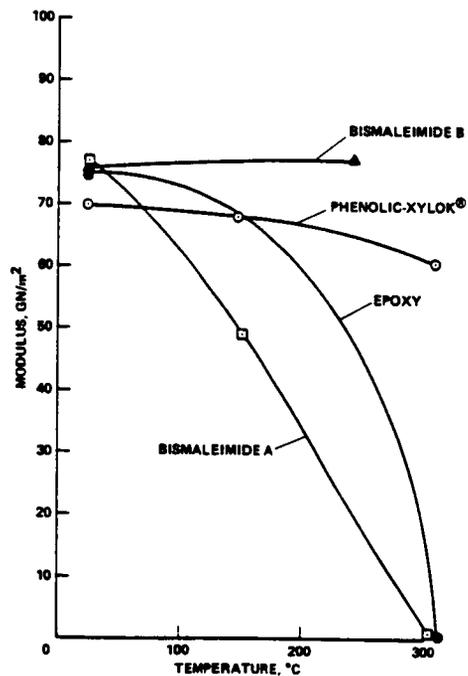


Figure 8. - Plot of modulus as function of temperature showing stability of bisimide B composite at temperatures which degrade both epoxy and bisimide A.

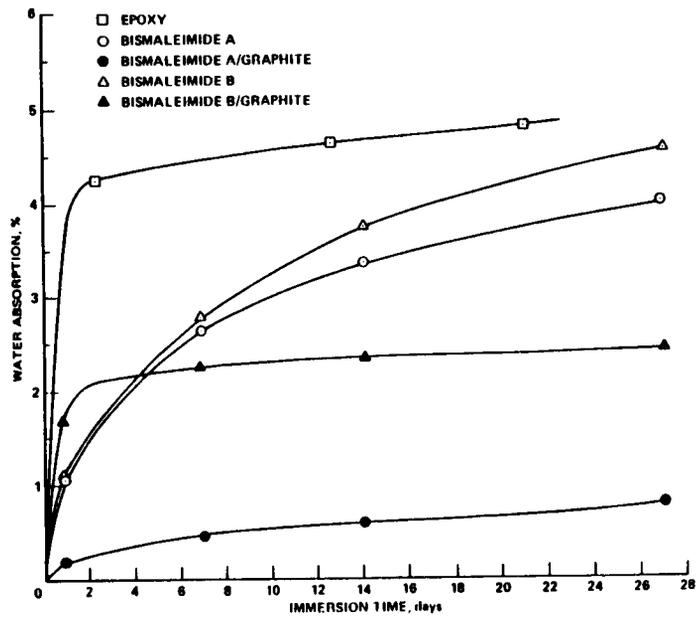


Figure 9. - Plot of water absorption as function of immersion time for bisimides and standard epoxides.

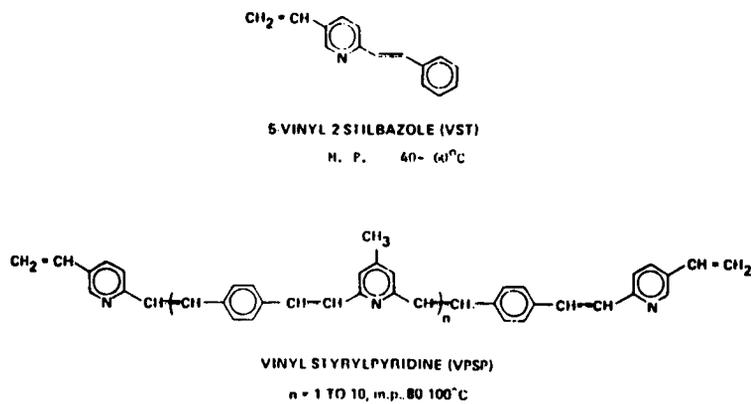


Figure 10. - Chemical structure of liquid oligomers.

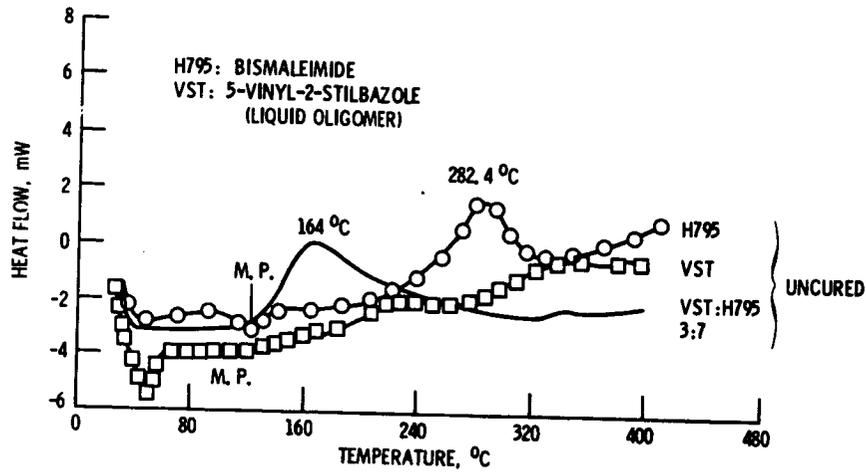


Figure 11. - DSC of bismaleimide (H 795) and VST/H 795 copolymers.

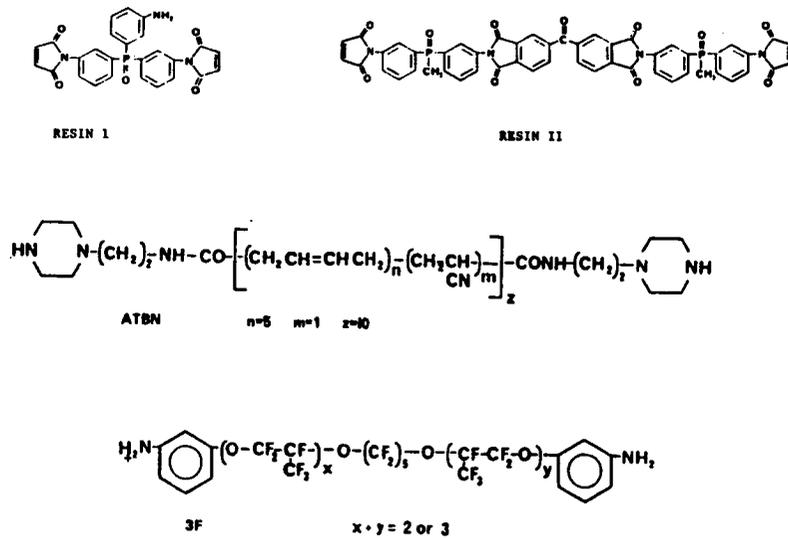


Figure 12. - Molecular structure of bismaleimide matrix resins prepared by replacing the methylene bridge with phosphonate linkages.

SCHEME I

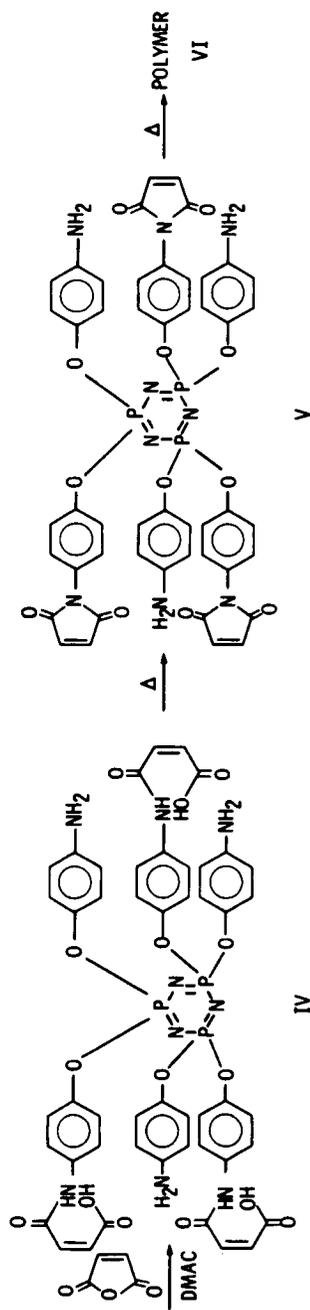
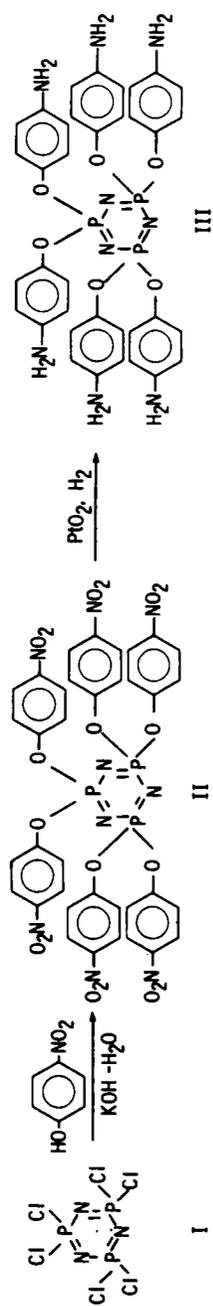


Figure 13. - Schematic showing the method for enhancing the stability of maleimido matrix resins with a thermally-stable tricyclic phosphazene moiety.

SCHEME II

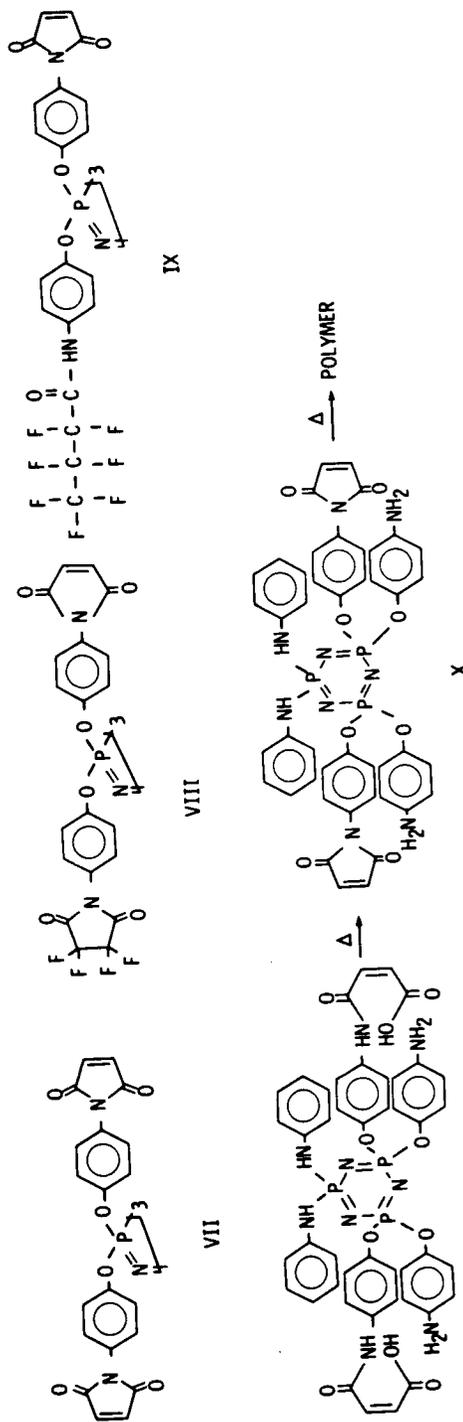


Figure 14. - Schematic showing additional variations of maleimido matrix resins.

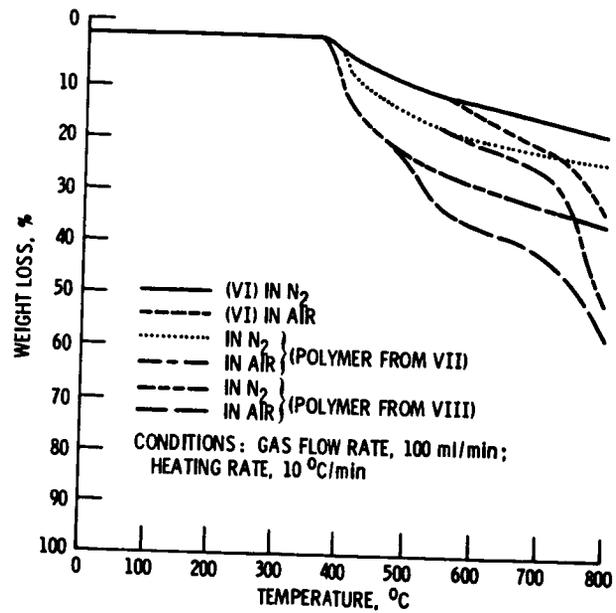


Figure 15. - Thermogravimetric analysis of cyclophosphazene polymers.

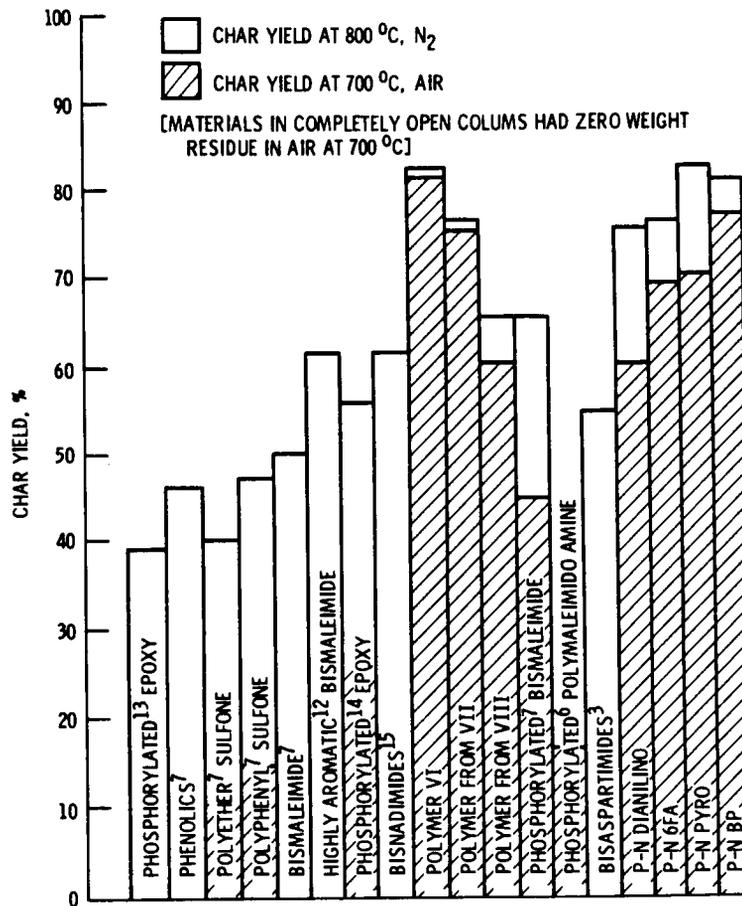


Figure 16. - Histogram comparing the thermal oxidative stability of tricyclophosphazenes with state-of-the-art bisimides and aromatic matrix resin polymers.

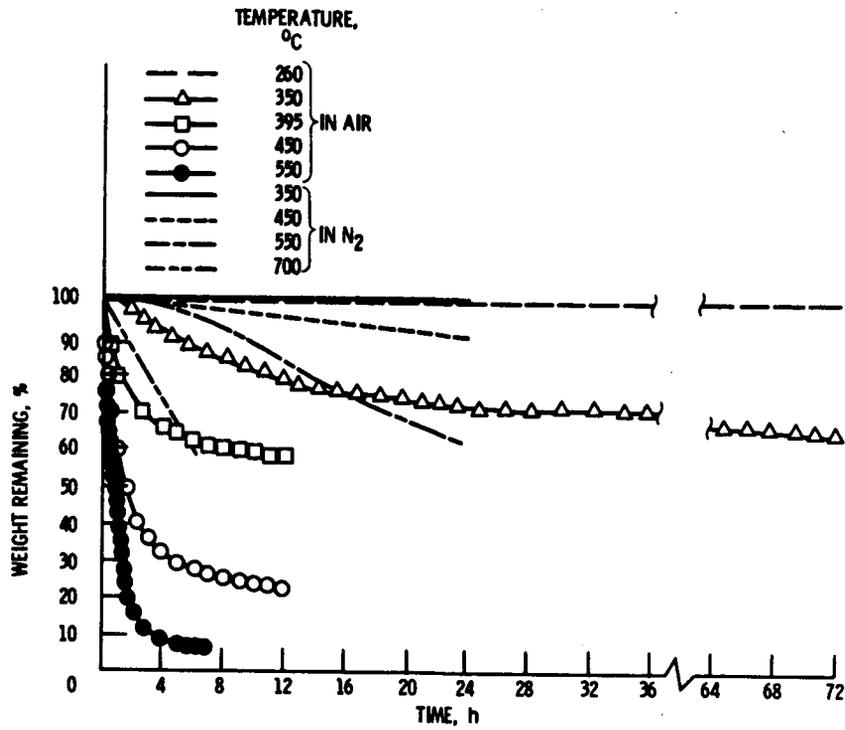


Figure 17. - Isothermal weight loss of (VI) at various temperatures.